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(Unclassified Title)

RESEARCH IN HIGH-ENERGY OXIDIZERS

First Quarterly Report

Fluorine Chemistry Unit
Chemistry Section
Research Division

Rocketdyne, a Division of North American Aviation, Inc.
6633 Canoga Avenue, Canoga Park, California
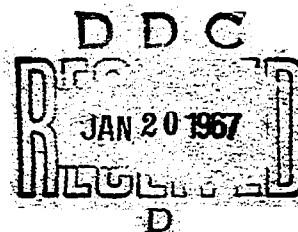
TECHNICAL REPORT AFRPL-TR-66-346

December 1966

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Group 4
Downgraded at 3-Year Intervals
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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California
Air Force Systems Command
United States Air Force

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FOREWORD

The work reported herein was performed under
Contract F04611-67-C-0007 and covers the
period 1 September 1966 through 30 November
1966. The program monitor is Lt. Charles
Stone (RPCL), Air Force Rocket Propulsion
Laboratory, Edwards Air Force Base, California.

The project scientist for the program is
Dr. D. Pilipovich, Principal Scientist of
the Fluorine Chemistry Unit. Full-time
personnel associated with the program are
Dr. W. Mara, Mr. R. D. Wilson, and Mr. M.
Warner. The prime program responsibility
is in the Synthetic Chemistry Group
(Dr. E. A. Lawton, Group Scientist) of the
Rocketdyne Research Division.

This report has been assigned the Rocket-
dyne identification number R-6840-1.

Publication of this report does not consti-
tute Air Force approval of the report's
findings or conclusions. It is published
only for the exchange and stimulation of
ideas.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

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ABSTRACT

The compound FCO_2NF_2 is being examined as a potential intermediate for the synthesis of other ONF_2 compounds. Techniques have been developed for handling FCO_2NF_2 to minimize its decomposition to F_2CO and FNO; the pre-treatment of containers with BF_3 is particularly advantageous in this regard. Compatibility studies of FCO_2NF_2 have revealed that it is stable to glass, steel, NO, O_2, and CO. Water catalyzes the decomposition of the compound and a typical mechanism has been postulated. When FCO_2NF_2 undergoes decomposition in the presence of C_2F_4, the latter does not participate in the reaction.

The ultraviolet spectrum of FCO_2NF_2 shows an end absorption commencing at 2100 angstroms. Fluorinations of FCO_2NF_2, with and without CsF, led only to the production of CF_3CF and nitrogen oxyfluorides. Preliminary experiments to effect condensation reactions of FCO_2NF_2 with $NaNO_2$ and $AgNO_2$ were attempted; only decomposition was observed. A reaction between FCO_2NF_2 and sodium trifluoroacetate in trifluoroacetyl anhydride solvent led to the formation of CF_3CFO and CF_3CO_2NO.

The reaction of CF_3CO_2NO with N_2F_4 in the presence of ultraviolet radiation led to the formation of $CF_3NO=NF$. With $ClNF_2$, CF_3CO_2NO gave CF_3CFO, NOCl, and N_2F_4 as the principal products, which are shown to have arisen probably via the formation of $CF_3CO_2NF_2$.

The photolysis of mixtures of trifluoroacetyl anhydride and N_2F_4 resulted in the formation of CF_3NF_2.

The synthesis of tetrafluorourea from perfluoroforma-
mide and KF has been examined, and this reaction
involves a labile NF_2 group of potential utility as
a new synthetic tool. The interaction of trifluoro-
acetyl anhydride with the KF complex of perfluoro-
formamide led to the formation of CF_3CONF_2. The
nature of the complex between KF and excess
perfluoroformamide was examined, and it has been
demonstrated that after aging at −40 C the complex
present is probably that of tetrafluorourea and KF.

(Confidential Abstract)

CONTENTS

INTRODUCTION

This is the first quarterly report on a research program designed to
exploit the use of the ONF_2 oxidizing group in high-energy oxidizer can-
didates. Previous work under other contracts, had resulted in the prep-
aration of $CF_2(ONF_2)_2$ (Ref. 1) and $FOCF_2ONF_2$ (Ref. 2). In addition, it
had been shown that, with $CF_2(ONF_2)_2$, no sensitivity problem existed
(Ref. 2) and this stability was expected to be conferred on higher homo-
logs. Thus, the principal aim of this present program is to seek methane
derivatives with three or four ONF_2 oxidizing groups.

Effort during the first quarter was concentrated on a study of the use
of perfluoroacyl nitrites as model compound intermediates in the forma-
tion of acyl ONF_2 derivatives. In addition to describing the results in
this area, this report also covers in detail the initiation of a concen-
trated study of the chemistry of difluoroaminoxycarbonyl fluoride and
perfluoroformamide. The potential of both of these intermediates will be
discussed in detail with respect to their utility in preparing more ener-
getic oxidizers.

DISCUSSION

THE CHEMISTRY OF DIFLUOROAMINOXY CARBONYL FLUORIDE, FCO_2NF_2

Difluoroaminoxy carbonyl fluoride is a potential intermediate for the synthesis of ONF_2 compounds provided the fluorocarbonyl group can be utilized synthetically without cleaving the ONF_2 group. This compound has been synthesized (Ref. 2), by the reaction of bis-(fluorocarbonyl) peroxide (Ref. 3) and N_2F_4 in the presence of a small amount of BF_3:

$$\underset{\text{FCOOCF}}{\overset{\text{O O}}{\|\ \|}} + N_2F_4 + BF_3 \longrightarrow 2\underset{\text{FCONF}_2}{\overset{\text{O}}{\|}} + BF_3$$
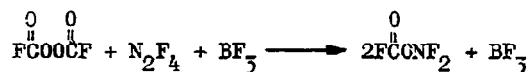
Although the BF_3 does not enter into the reaction, it presumably acts as a stabilizer for FCO_2NF_2; this latter compound has been found to decompose rapidly according to the following equation:

$$\underset{\text{FCONF}_2}{\overset{\text{O}}{\|}} \longrightarrow F_2CO + FNO$$

The presence of BF_3 does not prevent this decomposition from taking place, but it has been found to lessen the frequency. Infrequently, pure FCO_2NF_2 has been found to be stable in glass for long periods of time. However, once the FCO_2NF_2 starts to decompose, either pure or in mixtures with BF_3, the decomposition cannot be arrested and is complete in a matter of minutes. The instability of FCO_2NF_2 has been a barrier to the facile development of the chemistry of FCO_2NF_2. The compound has been, at times, so unstable that little more than its infrared spectrum could be determined before decomposition began. Thus, to utilize this compound, its handling aspects have been studied in detail and have progressed to the point where meaningful studies can be initiated.

Compatibility Studies

Mixtures of FCO_2NF_2 containing 10-percent BF_3 have limited stability in glass and in stainless steel. Traces of water are enough to cause the decomposition of a large amount of FCO_2NF_2. A small amount of water vapor was admitted into an infrared cell containing FCO_2NF_2 and BF_3. The spectrum, taken immediately afterward, showed only the disappearance of the BF_3. On admitting a further small amount of water vapor, the FCO_2NF_2 decomposed immediately before the spectrum could be recorded. Decomposition of FCO_2NF_2 has been observed with sodium fluoride but this experiment did not determine whether the sodium fluoride initiated the decomposition or merely caused it by removal of the BF_3.

Ultraviolet Spectrum of FCO_2NF_2

The ultraviolet spectrum of FCO_2NF_2, containing 10-percent BF_3, was taken to ascertain whether this compound is suited to photochemical reactions. The spectrum of the gas at 400 millimeters showed only an end absorption at 2100 angstroms; it is therefore concluded that light does not initiate the facile decomposition of FCO_2NF_2.

Mechanism of Decomposition

Difluoroaminoxycarbonyl fluoride has been found to be unreactive with NO, O_2, CO, and C_2F_4. With C_2F_4, the possibility existed that decomposition intermediates of FCO_2NF_2 might have added to the olefin:

$$C_2F_4 + FCO_2NF_2 \xrightarrow{\quad ? \quad} FCOCF_2CF_2ONF_2$$
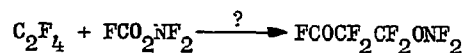
However, the FCO_2NF_2 was found to decompose in the presence of C_2F_4 without affecting the latter. This result, together with the unreactivity of FCO_2NF_2 towards NO and O_2, indicates there is no chain radical mechanism for the decomposition of FCO_2NF_2. Otherwise, it would be expected that O_2 or NO would have catalyzed the decomposition, or that CO or C_2F_4 would have acted as radical traps.

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A mechanism for the decomposition of FCO_2NF_2 is not immediately apparent but probably includes a base catalysis step. Water would hydrolyze the acyl halide but a propagation step is not readily obvious:

$$FCO_2NF_2 + H_2O \longrightarrow 2HF + CO_2 + FNO$$
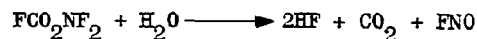
A specific base catalyzed reaction may involve the F^- as follows:

$$F^- + FCONF_2 \longrightarrow F_2CO + [ONF_2]^-$$

$$[ONF_2]^- \longrightarrow FNO + F^-$$

Here, both initiation and propagation steps are immediately obvious.

Handling Method

In an attempt to rigorously exclude moisture, bases, and active hydrogen sources from coming into contact with FCO_2NF_2, all apparatus used was p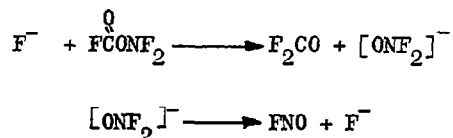retreated with BF_3. Thi. practice has been effective, and it is now possible to handle FCO_2NF_2 containing 10-percent BF_3 for extended periods without decomposition.

Fluorination of FCO_2NF_2

The fluorination of FCO_2NF_2 was undertaken to determine whether the known compound $FOCF_2ONF_2$ (Ref. 2) could be synthesized in this manner:

$$FCO_2NF_2 + F_2 \xrightarrow{\quad ? \quad} FOCF_2ONF_2$$
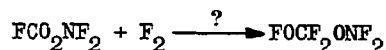
A total of 10 fluorinations were performed and are summarized in the experimental section of this report. Under a variety of conditions, the only products found were CF_3OF and nitrogen oxides and oxyfluorides.

However, it is not clear at this time whether the CF_3OF formed is a primary product, or whether it results from the fluorination of the decomposition product of FCO_2NF_2, i.e., COF_2:

$$F_2C=O + F_2 \longrightarrow CF_3OF$$

This question probably will be resolved during future work at Rocketdyne as more experience and knowledge is gained concerning the properties of FCO_2NF_2.

Condensation Reactions

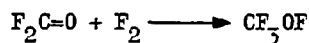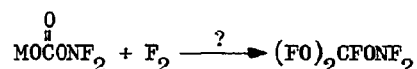A promising possibility is the formation of a salt, MO_2CONF_2 (where M is a metal) from FCO_2NF_2. Such a salt could lead to trifunctional fluoromethanes:

$$MO\overset{O}{\overset{\|}{C}}ONF_2 + F_2 \overset{?}{\longrightarrow} (FO)_2CFONF_2$$

Because FCO_2NF_2 is unstable in the presence of compounds containing an active hydrogen, indirect approaches to the formation of the salts have been undertaken. One approach involved the projected synthesis of an acyl nitrite, F_2NOCO_2NO, from FCO_2NF_2. Acyl nitrites are known to undergo reaction with metal halides to give the corresponding carboxy salts (Ref. 4):

$$CF_3CO_2NO + NaCl \longrightarrow CF_3CO_2Na + ClNO$$
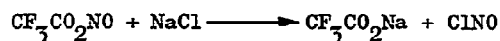
Another approach consists in the synthesis of a mixed anhydride from FCO_2NF_2, such as $CF_3CO_2CO_2NF_2$. Anhydrides can lead to salts either by reaction with salts (Ref. 5):

$$CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CF_3 + CsF \longrightarrow CF_3CO_2Cs + CF_3CFO$$
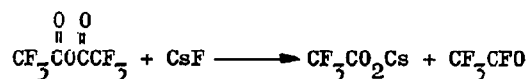
or by the intermediate formation of acyl nitrites, which are formed in high yield from the reaction of anhydrides with N_2O_3 (Ref. 6):

$$CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CF_3 + N_2O_3 \longrightarrow 2CF_3CO_2NO$$

6
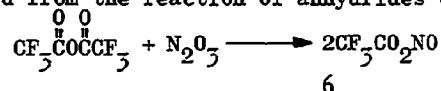
Both approaches have been examined cursorily during this period. The reactions of FCO_2NF_2 with $NaNO_2$ and $AgNO_2$ were attempted:

$$FCO_2NF_2 + MNO_2 \quad \xrightarrow{\quad\quad} \quad MF + ONO\overset{\overset{O}{\|}}{C}ONF_2$$
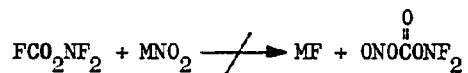
With both salts, the FCO_2NF_2 quickly decomposed to F_2CO and FNO. A more suitable reaction environment will be provided through the use of solvents. Accordingly, a search for solvents for FCO_2NF_2 was initiated. The first successful candidate is trifluoroacetic anhydride inasmuch as FCO_2NF_2 was recovered from it after 45 minutes at room temperature with a minimum of decomposition. The synthesis of a mixed anhydride was attempted by the reaction of FCO_2NF_2 with sodium trifluoroacetate in trifluoroacetic anhydride as the solvent. The principal products of the reaction were CF_3CFO and CF_3CO_2NO; both products are thought to arise by the interaction of trifluoroacetic anhydride with FNO formed during the reaction:

$$CF_3\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CF_3 + FNO \xrightarrow{\quad\quad} CF_3CFO + CF_3CO_2NO$$
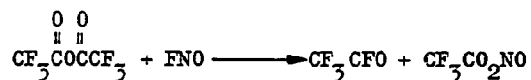
The presence of any moisture or free acid in the anhydride would make a fluoride ion available to the system, and fluoride ions, as discussed previously, may catalyze the decomposition of FCO_2NF_2 to form FNO. Future work will entail the use of other solvents, and emphasis will be placed on ensuring the removal of all traces of substances containing active hydrogen from the system.

REACTIONS OF TRIFLUOROACETYL DERIVATIVES

The reactions of trifluoroacetyl compounds with N_2F_4 have been studied as models (Ref. 3) for possible routes to the synthesis of homologs of FCO_2NF_2 compounds.

Reactions of Trifluoroacetyl Nitrite

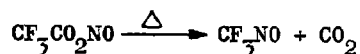Trifluoroacetyl nitrite was selected for this study because of its well-known thermal dissociation (Ref. 7):

$$CF_3CO_2NO \xrightarrow{\Delta} CF_3NO + CO_2$$

This indicated that the intermediate $CF_3CO_2\cdot$ radical may exist briefly during the dissociation. With N_2F_4 present during this process, the formation of $CF_3CO_2NF_2$ becomes a distinct possibility.

Thermal reactions between CF_3CO_2NO and N_2F_4, run in static systems at 70 C and in flow systems at 180 C, led to complete recovery of the starting materials.

Thermal reactions were abandoned in favor of ultraviolet excitation. The photolysis of CF_3CO_2NO led to the formation of CF_3NO and CO_2, completely analogous to the thermal process. Concurrent with this work, a study of the photolysis of CF_3CO_2NO appeared in Ref. 8 which presented essentially the same results. When mixtures of CF_3CO_2NO, N_2F_4, and BF_3 (to stabilize any $CF_3CO_2NF_2$ formed) were photolyzed, the main product was $CF_3NO=NF$, which is known to arise whenever NO, N_2F_4, and CF_3 radicals are present (Ref. 5 and 9):

$$CF_3CO_2NO \longrightarrow CF_3\cdot + NO + CO_2$$

$$CF_3\cdot + NO + N_2F_4 \longrightarrow CF_3\overset{O}{\underset{|}{N}}=NF + NF_3$$
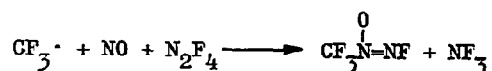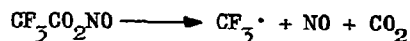
These results indicate that the decomposition of the radical $CF_3CO_2\cdot$ to the $CF_3\cdot$ radical and CO_2 is fast enough to preclude the formation of $CF_3CO_2NF_2$, at least under the experimental conditions used. No further work is contemplated on this approach at this time.

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The reaction of CF_3CO_2NO with $ClNF_2$ was also considered as a route to $CF_3CO_2NF_2$:

$$CF_3CO_2NO + ClNF_2 \xrightarrow{?} CF_3CO_2NF_2 + ClNO$$
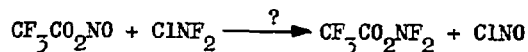
The reaction was carried out at room temperature for 20 hours; in addition to starting materials, products obtained were $NOCl$, CF_3CFO, N_2F_4, NO_2, a trace of SiF_4, and probably Cl_2, identified tentatively by its color and volatility. The formation of these products can be accounted for easily if the transitory formation of $CF_3CO_2NF_2$ is postulated with its facile decomposition to CF_3CFO and FNO (analogous to the behavior of FCO_2NF_2). The presence of FNO probably would not be detected under these conditions, because it would, by attacking the glass, be present as $(NO)_2SiF_6$. Other routes to the formation of CF_3CFO are not immediately apparent, because CF_3CO_2NO is known to cleave easily to give NO, but not NO_2. The formation of CF_3CFO would imply the unlikely cleavage:

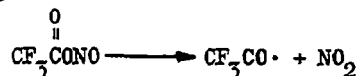$$CF_3\overset{O}{\overset{\|}{C}}ONO \longrightarrow CF_3CO\cdot + NO_2$$

Ionic attack of fluorides on the nitrite also would not lead to the formation of CF_3CFO, but to the formation of acetate salts (Ref. 4):

$$CF_3CO_2NO + MF \longrightarrow CF_3CO_2M + FNO$$
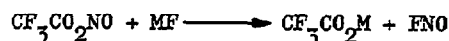
Reaction of Trifluoroacetic Anhydride

The photolysis of mixtures of trifluoroacetic anhydride and N_2F_4 were examined as a route to $CF_3CO_2NF_2$:

$$CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CF_3 + N_2F_4 \xrightarrow{?} CF_3CO_2NF_2 + CF_3\overset{O}{\overset{\|}{C}}NF_2$$
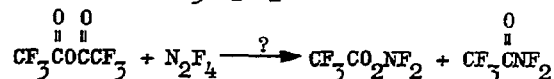
The result of a first attempt was the formation of CF_3NF_2, CO_2, and a carbonyl compound, probably CF_3CFO. The CF_3NF_2 was identified by its infrared spectrum (Ref. 10). This reaction constitutes a novel synthesis of CF_3NF_2, and although an exhaustive literature search has not been made,

appears to constitute the first instance of a photochemical reaction of trifluoroacetic anhydride. The formation of CF_3NF_2 implies that the radical $CF_3CO_2\cdot$ was formed, but that it is too unstable to react with N_2F_4 prior to decomposition.

CHEMISTRY OF PERFLUOROFORMAMIDE

The chemistry of perfluoroformamide leading to $(NF_2)_2CO$, reported by Frazer and Shreeve (Ref. 11) offers a number of possibilities for exploitation. The tetrafluorourea itself is of interest as an intermediate in the synthesis of a novel oxidizer containing both NF_2 and ONF_2 groups:

$$(NF_2)_2C=0 + F_2 \xrightarrow[?]{CsF} (NF_2)_2CFOF \xrightarrow{HNF\cdot KF} (NF_2)_2CFONF_2$$
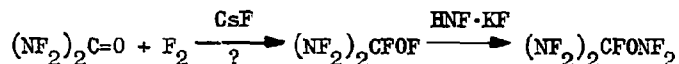
The resulting compound could be examined for any attenuating effect of the ONF_2 group on the sensitivity of the $C(NF_2)_2$ group.

An understanding of the chemistry and the techniques of the tetrafluorourea synthesis which could be extended to other systems aimed at the synthesis of new $CONF_2$ compounds is of immediate interest. The synthesis reported by Frazer and Shreeve seems to consist of two steps: (1) formation of a difluoroaminocarbonyl fluoride-KF complex, and (2) pyrolysis of the complex:

$$F_2NCFO + KF \longrightarrow F_2NCFO\cdot KF \xrightarrow{\triangle} (F_2N)_2CO + \text{---}$$

An interesting aspect of these reactions is the implied migration of an NF_2 group from one carbon atom to another, either by a concerted or stepwise mechanism, which could be of wide synthetic utility.

An initial attempt to repeat this work resulted in an explosive decomposition of the complex during pyrolysis, an anticipated event which affirmed that proper techniques were used in the complexing step. The complexing step was then studied in greater detail, resulting in the following facts.

1. Complexing of F_2NCFO and KF does not take place in a heterogeneous system, but does take place in a vigorously anhydrous acetonitrile solvent.

2. Success of the synthesis of the complex depends on the use of excess F_2NCFO, ideally 2 moles of F_2NCFO per mole of KF, and allowing sufficient time (1 or more days) for the complexing step at -40 C in acetonitrile.

3. The complexing step is accompanied by the evolution of F_2CO corresponding to approximately one-half of the total amount of F_2NCFO.

Thus, the solid complex obtained after removal of volatile material may be of the composition indicated in the following equation:

$$F_2NCFO + \left[F_2NCF_2O\right]^-K^+ \xrightarrow{CH_3CN} F_2CO + \left[(F_2N)_2FCO\right]^-K^+$$
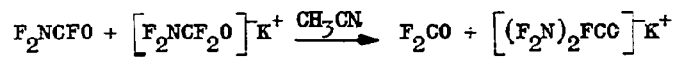
Smooth decomposition of the underlined complex should give tetrafluorourea and KF.

An attempt was made to displace tetrafluorourea from the complex with AsF_5:

$$\left[(F_2N)_2FCO\right]^-K^+ + AsF_5 \xrightarrow{\quad/\quad} (F_2N)_2CO + KAsF_6$$
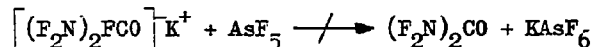
However, there was no reaction upon contact of gaseous or liquid AsF_5 with the complex, demonstrating the reduced reactivity of the complex in the absence of a solvent. The complex was treated with trifluoroacetic anhydride in an attempt to effect the displacement:

$$\left[(F_2N)_2FCO\right]^-K^+ + (CF_3CO)_2O \xrightarrow{\quad?\quad} CF_3CFO + CF_3CO_2K + (F_2N)_2CO$$
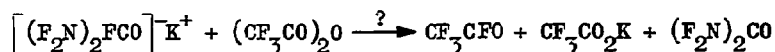
The major volatile products obtained from the reaction consisted of CF_3CONF_2 and CF_3CFO, the combined amounts of which nearly corresponded to the initial amount of F_2NCFO used. Also obtained were smaller amounts of HNF_2, CO_2, and CF_3CO_2H indicative of moisture contamination. No perfluorourea was found. Although the presence of moisture complicated the results, the formation of CF_3CONF_2 suggests a $\overline{NF_2}$ anion transfer from

what was probably the perfluorourea and KF complex. The following equation depicts the apparent course of reaction between the complex of tetrafluorourea and KF and trifluoroacetic anhydride contaminated with moisture:

$$\left[(F_2N)_2FCO\right]^- K^+ \; (CF_3CO)_2O \; + \; CF_3CO_2H \longrightarrow CF_3\overset{\overset{\displaystyle O}{\|}}{C}NF_2 \; +$$

$$CF_3COF \; + \; CF_3CO_2K \; + \; HNF_2 \; + \; CO_2$$
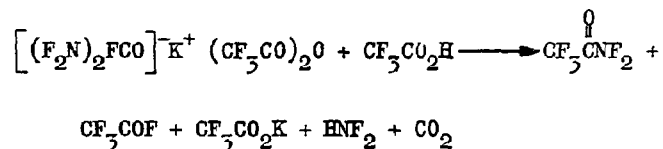
The formation of HNF_2 is the expected consequence of the action of a proton displacing the metal ion from the complex, and subsequent elimination of HNF_2:

$$F_2C\overset{\displaystyle OK}{\underset{\displaystyle NF_2}{\big\langle}} \;\; \xrightarrow{\;H^+\;} \;\; \left[F_2C\overset{\displaystyle OH}{\underset{\displaystyle NF_2}{\big\langle}}\right] \longrightarrow F_2C{=}O \; + \; HNF_2$$
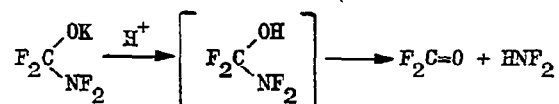
The observed transfer of NF_2^- anion in the trifluoroacetic anhydride reaction helps substantiate the contention that a very similar process occurred in the synthesis of perfluorourea itself, which may be more simply depicted by two equilibria involving solvated species:

$$F_2NCF_2O^- \; \underset{\longleftarrow}{\overset{CH_3CN}{\longrightarrow}} \; NF_2^- \; + \; F_2CO$$

$$NF_2^- \; + \; F_2NCFO \; \underset{\longleftarrow}{\overset{CH_3CN}{\longrightarrow}} \; (F_2N)_2FCO^-$$
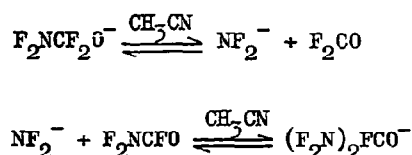
or the process can be visualized as a concerted displacement:

$$F - \overset{\overset{\displaystyle O}{}}{\underset{\displaystyle F}{C}}\!\!-\!\!NF_2 \;\; + \;\; \overset{\displaystyle F}{\underset{\displaystyle NF_2}{{\big\backslash}}}C{=}O \longrightarrow F_2CO{+}F_2N{-}\overset{\overset{\displaystyle F}{}}{\underset{\displaystyle O^-}{C}}\!\!-\!\!NF_2$$
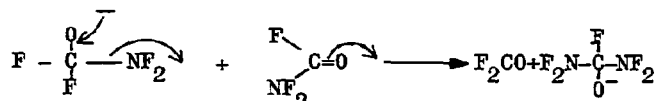
Significant, also, is the observation that CO_2 and not F_2CO was produced in the trifluoroacetic anhydride reaction, indicating that the reactive species could not have been $(F_2NCF_2O)^- K^+$, which would have produced F_2CO:

$$F_2NCF_2O^- \; + \; (CF_3CO)_2O \longrightarrow CF_3\overset{\overset{\displaystyle O}{\|}}{C}NF_2 \; + \; CF_3CO_2^- \; + \; F_2CO$$
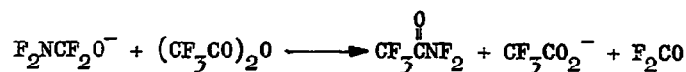
At least some F_2CO, if produced, should have survived even the moisture-contaminated trifluoroacetic anhydride.

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Future plans include direct fluorinations of the perfluorourea and KF complex, further exploration of the NF_2 transfer phenomenon, and extension of the perfluorourea synthesis techniques to other systems.

EXPERIMENTAL

CHEMISTRY OF FCO_2NF_2

Preparation of $F_2C_2O_4$

Bis-(fluorocarbonyl) peroxide was prepared by the action of fluorine on CO and O_2 (Ref. 3).

Preparation of FCO_2NF_2

A 300-milliliter Pyrex ampoule fitted with either a high-vacuum stopcock or a Fisher-Porter valve was flamed out and pretreated with approximately 400 millimeters of BF_3. The ampoule was loaded by condensation with $F_2C_2O_4$ (50 cc), N_2F_4 (50 cc), and approximately 10 cc of BF_3. The ampoule was stored at room temperature for 2 days; at the end of this period the infrared spectrum of the material revealed almost complete reaction to FCO_2NF_2, and the BF_3 was still present. Arsenic pentafluoride was also employed in the place of BF_3, but did not offer any advantage. The yields of FCO_2NF_2 were of the order of 80 percent.

Fluorination of FCO_2NF_2

The fluorinations were conducted in Type 304 stainless-steel Hoke cylinders fitted with stainless-steel valves, that had been passivated with fluorine for a minimum of 12 hours. The fluorinations are listed in Table 1 . In a typical preparation, the CsF it employed was loaded in a dry box. The FCO_2NF_2 (30 to 40 cc) was condensed into the cylinder and an appropriate amount of fluorine was condensed in at -196 C. The cylinder was placed in a bath made from a slurry of Dry Ice powder and liquid nitrogen, and allowed to warm gradually to -80 C. After the specified reaction time, the fluorine was pumped off at -196 C, and the remainder of the reaction mixture was worked up in the usual manner in a glass high-vacuum line.

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TABLE 1

FLUORINATION OF $FCONF_2$*

Fluorination No.	Cylinder volume, milliliters	Fluoride Used	Approximate Volume of Fluorine	Reaction Temperature, °C	Reaction Time	Products
1	30	5 grams of CsF	1 liter	-80	3 days	CF_3OF, NO_2, NOF, FNO_2
2			1 liter		4 days	CF_3OF, NO_2, NOF, FNO_2
3			No fluorine (control experiment)		~16 hours	Recovered unreacted $FCONF_2$, COF_2, FNO, FNO_2
4			1 liter		~16 hours	CF_3OF, NO_2
5		5 grams of CsF			2 days	CF_3OF, NO_2
6		5 grams of CsF	100 cc		~16 hours	Unreacted FCOOCF and N_2F_4 / CF_3OF, NO_2, trace of unknown
7			100 cc		~16 hours	The $FCONF_2$ was recovered and reused
8**			500 cc		3 days	CF_3OF, NO_2, trace of FCOOCF
9			500 cc		5 days	COF_2, FNO, NO_2, trace of FCOOCF, BF_3, trace of unknown
10		5 grams of CsF	500 cc		6 days	CF_3OF, NOF, N_2F_4, COF_2, trace of FCOOCF, trace of unknown

*Reactant $FCONF_2$ was used directly from preparation, and in some cases contained unreacted FCOOF, N_2F_4, and BF_3.

**Reused $FCONF_2$ from reaction 7

REACTIONS OF TRIFLUOROACETYL DERIVATIVES

Synthesis of CF_3CO_2NO

Trifluoroacetyl nitrite was synthesized by the reaction of N_2O_3 and the anhydride (Ref. 6).

Photolysis Reactions

The photolysis reactions were conducted in Vycor and quartz vessels, and the irradiations were performed at room temperature with a Hanovia Utility Lamp, Type 30620, rated at 140 watts. The products were analyzed by infrared spectroscopy after trap-to-trap distillation in a high-vacuum line.

CHEMISTRY OF PERFLUOROFORMAMIDE

Preparation

The ultraviolet-initiated reaction of CO and N_2F_4 was carried out as reported by Frazer and Shreeve (Ref. 12) except that higher yields were obtained (25 to 30 percent) through the use of an air-cooled, low-pressure mercury vapor Hanovia Utility Lamp, Type 30620, and an ice water-cooled 2-liter reactor flask.

Preparation of Activated Potassium Fluoride

A special apparatus was fabricated for the purpose of depositing a measured amount of activated KF in a reaction flask. The operation consisted of passing gaseous hexafluoroacetone (HFA) into a suspension of fusion-dried KF in anhydrous acetonitrile at -30 C. The resulting solution of the KF·HFA complex in acetonitrile was forced through a sintered glass filter

and into the reactor. The solvent was then pumped off and the complex decomposed by warming it to 100 C, leaving an amount of activated KF which closely corresponds to the quantity of hexafluoroacetone used. One mmole of hexafluoroacetone measured by flowmeters delivers approximately 0.87 mmole of KF.

Complex Formation

Into a 200-milliliter Pyrex reactor containing activated KF (1.1 mmoles) was condensed F_2NCFO (50 cc) and anhydrous acetonitrile (approximately 3 milliliters). The mixture was stored at -40 C for several days. Removal of volatile material at 0 C and fractionating through -80, -142, and -196 C traps gave CF_2O (approximately 25 cc) and CH_3CN. No F_2NCFO was detected by infrared analyses. The white solid remaining in the reactor is believed to be the tetrafluorourea KF complex.

Attempted Displacement of TFU with AsF_5

To the previously described complex was added AsF_5 (50 cc) at -196 C. The mixture was warmed to room temperature and refrozen several times. The AsF_5 was recovered quantitatively. The ampoule was then reloaded with AsF_5 (350 cc) and thermostatted at -63 C for 4 hours. Again, the AsF_5 was recovered without reaction.

Reaction of TFU·KF Complex With $(CF_3CO)_2O$

To the ampoule containing the TFU·KF complex was added $(CF_3CO)_2O$ (215 cc) and the mixture was maintained at 0 C overnight. Fractionation and infrared analysis of the volatile products revealed CF_3CONF_2 (22 cc), CF_3COF (22 cc), HNF_2 (5 cc), CO_2 (6 cc), and unreacted $(CF_3CO)_2O$. The solid residue was heated to 100 C with pumping only to yield a small amount of CF_3COOH indicating moisture contamination of the reaction.

REFERENCES

1. AFRPL-TR-65-172, Annual Report, Research in High-Energy Oxidizers, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, October 1965, CONFIDENTIAL.

2. AFRPL-TR-66-219, Final Report, Research in High-Energy Oxidizers, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, October 1966, CONFIDENTIAL.

3. Arvia, A. J., P. J. Aymonino, and J. J. Schumacher, Z. anorg. allgem. Chem., 316, 327 (1962).

4. Taylor, C. W., T. J. Brice, and R. L. Wear, J. Org. Chem., 27, 1064 (1962).

5. AFFTC-TR-19, Development and Evaluation of Storable High-Energy Bipropellant Systems, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, Calif., April 1961, CONFIDENTIAL.

6. Rice, D. E. and G. H. Crawford, J. Org. Chem., 28, 872 (1963).

7. Park, J. D., R. W. Rosser, and J. R. Lacher, J. Org. Chem., 27, 1462 (1962).

8. Banks, R. E., M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, J. Chem. Soc., (c), 1350 (1966).

9. Frazer, J. W., R. K. Pearson, B. E. Holden, and E. F. Worden, J. Inorg. Nucl. Chem., 24, 45 (1962).

10. Pearson, R. K. and R. D. Dresdner, J. Am. Chem. Soc., 84, 4743 (1962).

11. Frazer, G. W. and J. M. Shreeve, Chem. Comm., 15, 532 (1966).

12. Frazer, G. W. and J. M. Shreeve, Inorg. Chem., 4, 1497 (1965).

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13. ABSTRACT

The compound FCO_2NF_2 is being examined as a potential intermediate for the synthesis of other ONF_2 compounds. Compatibility studies of FCO_2NF have revealed that it is stable to glass, steel, NO, O_2, and CO. Water catalyzes the decomposition of the compound and a typical mechanism has been postulated. When FCO_2NF_2 undergoes decomposition in the presence of C_2F_4, the latter does not participate in the reaction. Fluorinations of FCO_2NF_2, with and without CsF, led only to the production of CF_3OF and nitrogen oxyfluorides. Preliminary experiments to effect condensation reactions of FCO_2NF_2 with $NaNO_2$ and $AgNO_2$ were attempted; only decomposition was observed. The reaction of CF_3CO_2NO with N_2F_4 in the presence of ultraviolet radiation led to the formation of $CF_3NO=NF$. With $ClNF_2$, CF_3CO_2NO gave CF_3CFO, NOCl, and N_2F_4 as the principal products, which are shown to have arisen probably via the formation of $CF_3CO_2NF_2$. The photolysis of mixtures of trifluoroacetyl anhydride and N_2F_4 resulted in the formation of CF_3NF_2. The synthesis of tetrafluorourea from perfluoroformamide and KF has been examined, and this reaction involves a labile NF_2 group of potential utility as a new synthetic tool. The interaction of trifluoroacetyl anhydride with the KF complex of perfluoroformamide led to the formation of CF_3CONF_2. The nature of the complex between KF and excess perfluoroformamide was examined, and it has been demonstrated that after aging at -40 C the complex present is probably that of tetrafluorourea and KF. (C)

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